

# Chemistry–A European Journal

Supporting Information

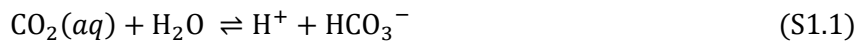
## **Calcium Carbonate Dissolution from the Laboratory to the Ocean: Kinetics and Mechanism**

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## Section 1: Carbonate Speciation

A lot of time and effort has gone into quantifying the thermodynamics associated with the carbonate system. In terms of the defining equilibria and how to solve these systems of equations we refer the reader to a number of well written reviews and textbooks on the subject.<sup>[1-3]</sup> However for clarity we summarise some important aspects here.

At equilibrium and in the absence of other species the following equations define the equilibrium concentration of the calcite ions in a solution in contact with solid calcite:



At equilibrium, and taking the activity of both water and calcite to be unity then the corresponding stoichiometric equilibrium constants are:

$$K_1^* = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (\text{S1.5})$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (\text{S1.6})$$

$$K_w = [\text{H}^+][\text{OH}^-] \quad (\text{S1.7})$$

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \quad (\text{S1.8})$$

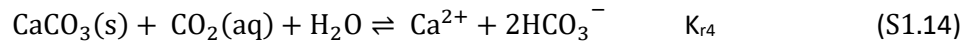
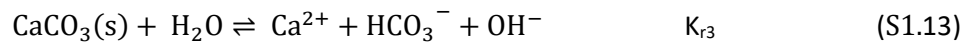
Here we have six unknown concentrations and so to solve this problem we need two additional auxiliary equations:

$$2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{OH}^-] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] \quad (\text{S1.9})$$

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CO}_2(aq)] \quad (\text{S1.10})$$

Equation S1.9 is a statement of electroneutrality and equation S1.10 is a statement of conservation of mass; for every calcium dissolved one carbon is added to the solution. Consequently, if we take the reported<sup>[1]</sup> thermodynamic constants that vary as both a function of solution temperature and salinity then equations S1.5-S1.10 present a series of 6 simultaneous equations to be solved. It is on this basis that the equilibrium ion concentrations for a closed system can be determined.

Usefully equations S1.1- S1.4 can be recast as:



these four equations are thermodynamically equivalent to those presented earlier and the associated thermodynamic constants are:

$$K_{r1} = K_{sp} \quad (\text{S1.15})$$

$$K_{r2} = \frac{K_{sp}}{K_2} \quad (\text{S1.16})$$

$$K_{r3} = \frac{K_{sp}K_w}{K_2} \quad (\text{S1.17})$$

$$K_{r4} = \frac{K_{sp}K_1^*}{K_2} \quad (\text{S1.18})$$

these four equations (S1.11- S1.14) represent four thermodynamic pathways that can, in the absence of other acid/base moieties in the solution, drive the calcite dissolution.

## Section 2: Surface vs Mass-Transport Control

Broadly for any interfacial process the rate determining step can be:

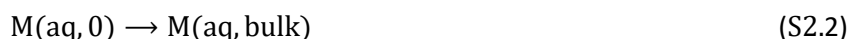
- a) Transport of reagents to the interface
- b) Reaction at the interface
- c) Transport of products away from the interface

Which of these processes is dominant depends on the stoichiometry of a given reaction, the rate of the interfacial reaction, the properties of the interface and also the prevailing mass-transport i.e. how fast the reagents and products can move to and away from the interface. In this section we are going to take a simple example of an interfacial reaction and show how physical changes to the system – in this case changing the particle radius – can change which step of the process is rate determining.

### Dissolution of a spherical particle

Here we consider the simplest dissolution process, a solid spherical particle of M dissolves into solution, where in the bulk solution the concentration of M is zero and importantly for this example *M is only sparingly soluble*. Here we will only consider the steady-state solution to this problem. For this example reaction, we only need to consider steps b) and c) from the list above.

Overall the reaction scheme is:



Equation S2.1 is the dissolution reaction leading to the formation of dissolved solution phase M, where 0 indicates that the species formed at the interface. Reaction S2.2 represents the transport of the M species away from the surface into the bulk solution. As we are assuming that the bulk concentration of M is zero then we do not need to consider the back reaction of process S2.2.

The rate of the dissolution reaction is ( $j_{diss}$  / mol m<sup>-2</sup> s<sup>-1</sup>):

$$j_{diss} = k_{diss} \quad (S2.3)$$

where  $k_{diss}$  is the zeroth order heterogeneous rate constant. The precipitation reaction i.e. the reverse of reaction S2.1 is given by:

$$j_{precip} = k_{precip}[M]_0 \quad (S2.4)$$

here  $k_{precip}$  has units of  $m\ s^{-1}$  and is a first order heterogeneous rate constant. As M is only sparingly soluble then we define the solubility as:

$$K_s = [M]_{sat} \quad (S2.5)$$

Consequently, at equilibrium:

$$j_{precip} = j_{diss} \quad (S2.6)$$

hence,

$$k_{precip} = \frac{k_{diss}}{K_s} \quad (S2.7)$$

As we are assuming that i) we have a spherical particle, ii) the bulk concentration of M is zero and iii) the system is at steady-state, then the rate associated with equations S2.2 is:

$$j_{MT} = \frac{D[M]_0}{r_p} \quad (S2.8)$$

where D diffusion coefficient ( $m^2\ s^{-1}$ ) and  $r_p$  is the radius of the particle (m). Given we are considering the steady-state situation then:

$$j_{diss} = j_{precip} + j_{MT} \quad (S2.9)$$

The above expression is essentially saying that the surface concentration of M is fixed and does not vary, in this case (the steady-state regime) the formation of dissolved M ( $j_{diss}$ ) is equal to its loss via precipitation ( $j_{precip}$ ) and mass-transport to the bulk ( $j_{MT}$ ). From equation S2.9 and substituting in equations S2.3, S2.4, S2.7 and S2.8 then we can get an expression describing the surface concentration of species M:

$$[M]_0 = \frac{k_{diss}K_s r_p}{k_{diss}r_p + DK_s} \quad (S2.10)$$

Substituting this expression into equation S2.8 then we get an expression describing the rate of dissolution of the particle:

$$j_{tot} = \frac{Dk_{diss}K_s}{k_{diss}r_p + DK_s} \quad (S2.11)$$

Clearly this is a simple model but there are some very important features of equation S2.11.

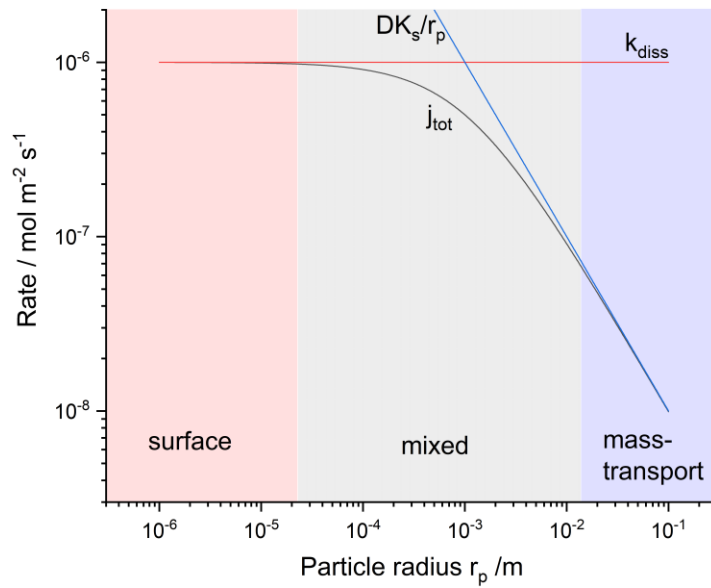


Figure S1: The variation in the heterogeneous interfacial rate as a function of particle size as predicted by equation 11 ( $j_{tot}$ , black line). For small particle radii the rate becomes surface controlled (red zone) and  $j_{tot} \approx k_{diss}$ , conversely for large particle radii the rate becomes mass transport limited (blue zone) and  $j_{tot} \approx DK_s/r_p$ . In between these two limits is a mixed kinetic regime (grey) where the interfacial rate is neither at the surface nor mass-transport controlled limit. For comparison the two limiting cases of  $k_{diss}$  and  $DK_s/r_p$  are also plotted in red and blue lines respectively. For this example:  $D = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $k_{diss} = 1 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ ,  $K_s = 1 \text{ mol m}^{-3}$ .

Figure S1 takes some example parameters and plots how the rate of dissolution of the particle changes as a function of the particle size (radius). As can be seen if the particle radius is small then rate of the reaction is controlled by the surface reaction rate ( $k_{diss}$ ) but as the size of the particle increases then the rate changes and becomes controlled by the mass-transport ( $D[M]_0/r$ ). Changing the physical size of the particle changes the rate determining step. When the rate is under mass-transport control then the dissolution rate ( $j_{tot}$ ) does not contain information about the magnitude of  $k_{diss}$ .

The above example is really important when we consider calcite dissolution, whether the reaction rate is under mass-transport or surface control can change depending on how quickly material can get to and from the mineral interface. This switch in behavior hinges on the fact that we are recognizing that the concentration of species at the interface can be different from that of the bulk solution. For an isolated micron sized particle this change in concentration occurs over the distance of about a particle radius from the mineral surface. This change in the surface concentration as a function of particle size is most clearly seen in considering equation S2.10. If the particle is small leading to the dissolution rate being under surface control then the  $[M]_0 \approx 0$ . Conversely, if the particle is large then  $[M]_0 \approx [M]_{sat}$  leading to the reaction being under mass-transport control.

## Section 3: Mass-transport correction

What is meant by ‘making a mass-transport correction’ as referred to in the main body of the text? Let us consider this in the context of the dissolution model presented in Section 1. As shown in Figure S1, if  $k_{diss} > DK_s/r_p$  then the interfacial dissolution rate is less than  $k_{diss}$  and in the limit the overall rate becomes equal to  $DK_s/r_p$ . This situation is known as the mass-transport limited regime. Conversely, when  $k_{diss} \approx DK_s/r_p$  then the overall rate ( $j_{tot}$ ) is less than either  $k_{diss}$  or  $DK_s/r_p$ . This transitional case is known as the ‘mixed kinetic regime’. When we are in this so-called mixed kinetic regime, is it possible to accurately determine the underlying value of  $k_{diss}$  from the measured dissolution rate? That is to say, can we ‘correct’ the experimentally determined dissolution rate so as to extract the true interfacial kinetics of the dissolution process ( $k_{diss}$ )? This question is essentially the same as asking; if the surface concentrations are unaltered from that of the bulk (i.e. for the example above if  $[M]_0 = [M]_{bulk} = 0$ ) then what is the rate of the dissolution reaction? This problem is directly analogous to the problem of extracting heterogeneous rate constants from an electrochemical experiment. Classically, in electrochemistry a rotating disc electrode is used and a Koutecky-Levich plot is used to infer the true rate constant for an interfacial reaction.

How accurately the measured rate ( $j_{tot} / \text{mol m}^{-2} \text{s}^{-1}$ ) can be corrected depends not only on the uncertainty in the measurement but how well the mass-transport regime is defined. Taking the above example of the steady-state flux from a particle isolated in the solution phase, then for a given measured interfacial rate, we can rearrange equation S2.11 to give an analytical expression that allows calculation of the ‘true’ heterogeneous rate constant ( $k_{diss} / \text{mol m}^{-2} \text{s}^{-1}$ ):

$$k_{diss} = \frac{Dj_{tot}K_s}{DK_s - r_p j_{tot}} \quad (\text{S3.1})$$

If the particle radius, molecular diffusion coefficient and solubility are known to a high degree of accuracy then equation S3.1 can be used to extract the heterogeneous rate constant for the dissolution reaction. It is important to reflect on the fact that equation S3.1 can only be used if the system is accurately modelled as a particle isolated in solution where the mass-transport to and from the interface only occurs via diffusion and there is no particle agglomeration/aggregation. The possible influence of convection and particle agglomeration/aggregation has not been considered and as discussed at length in the main body of the text, for some experimental cases these factors can have a significant influence on the measured rate. The accuracy of the mass-transport correction depends on the accuracy of the used model.

As will be explored further below (section 5) if the mineral particles are not well isolated in solution, as is the case for example in a sediment, then equation S2.11 cannot be applied. It perfectly possible

for the mass-transport limited reaction rate to be orders of magnitude below the true heterogeneous reaction rate.



## Section 4: Literature examples

In terms of studying calcite dissolution in genuine or artificial seawater samples one experimental problem is that at atmospheric pressure and room temperature most seawater-like samples are oversaturated with respect to calcite. Consequently, the only easily accessible experimental method to studying calcite dissolution in these solutions is to partially acidify them. For a solution containing 10 mM  $\text{Ca}^{2+}$  and 2.3 mM dissolved inorganic carbon then a pH of  $\sim 7.37$  is required for the solution to be at the saturation level. The addition of further acid will lead to the system being undersaturated. This is a commonly used technique where the rate of calcite dissolution is then measured in this acid adjusted undersaturated solution. One potential problem for this method is that the dissolution is not being studied at a pH comparable to the conditions under which dissolution occurs in the ocean. Further, there is often only a limited evidence that the system is not being studied at or near the mass-transport limit.

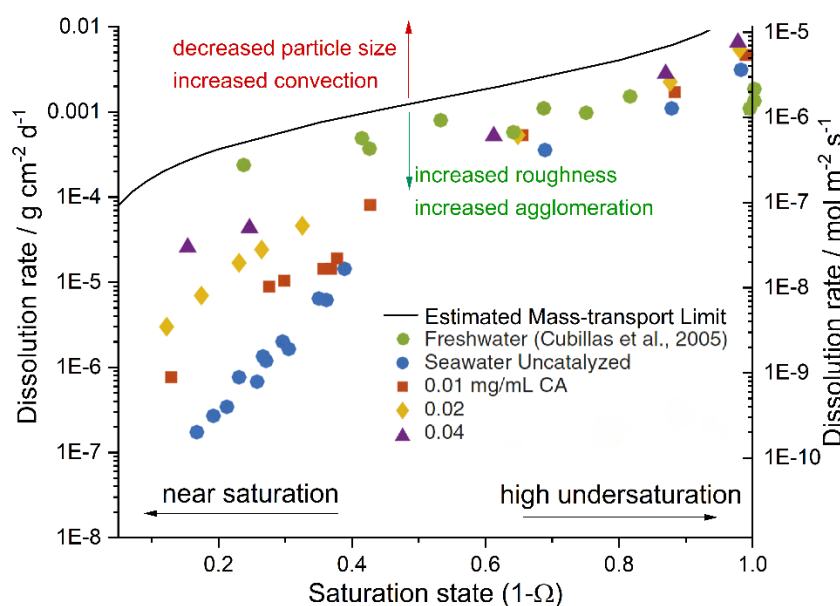


Figure S2: Calcite dissolution rate in artificial seawater as a function of undersaturation state and the influence of the addition of carbonic anhydrase (CA).  $\Omega$  is the saturation state of the solution with respect to calcite. Data reproduced with permission from Subhas et al. (2017)<sup>[4]</sup> (Copyright 2017 National Academy of Sciences). Overlaid on the original experimental data is the dissolution rate predicted for a diffusion limited flux away from the particles with an assumed diffusion layer thickness of 100  $\mu\text{m}$  (black line). This estimate of the mass-transport limit is subject to significant uncertainty as discussed in the text and as highlighted in the figure the exact value is altered by the physical state of the system. Importantly however, at high undersaturation even in this artificial seawater media the dissolution rate is apparently at least comparable to the mass-transport limited flux (a mixed kinetic regime). Indicating that accurate determination of the interfacial reaction rate under these conditions may require mass-transport correction of the measured rate.

For example, in the work of Subhas *et al.* the dissolution of a suspension of  $^{13}\text{C}$  labelled calcite particles is studied in an artificial seawater sample.<sup>[4]</sup> The solution was acidified so as to adjust the saturation state of the sample. One of the key results of this work is reproduced in Figure S2, where the authors of the original work demonstrate that at all calcite saturation levels ( $\Omega$ ) the dissolution kinetics are sensitive to the presence and concentration of carbonic anhydrase suggesting that under these conditions the hydration kinetics of  $\text{CO}_2$  is important in controlling the dissolution rate. However, if we assume a diffusion layer thickness of  $100\text{ }\mu\text{m}$  then we can see that at high under saturation the reported data seems to be approaching the estimated mass-transport limit and this may give physical insight into why the reaction is less sensitive to the presence of carbonic anhydrase at high undersaturation. Note that these high undersaturation results are essentially comparable to measurements independently made by Cubillas *et al.* in a fresh water sample.<sup>[5]</sup> As discussed in detail in the main text, due to ambiguities in the mass-transport properties of the system quantitative analysis of the mass-transport limited flux is challenging where differences in the particle size, surface roughness, agglomeration state and the influence of convection can all alter the expected flux. This issue is compounded in the work of Subhas *et al.*<sup>[4]</sup> where they do not explicitly state the used particle grain size in the text however on the basis of their cited previous work<sup>[6]</sup> where particles in the range of  $70\text{-}700\text{ }\mu\text{m}$  are used then a value of  $100\text{ }\mu\text{m}$  for the diffusion layer thickness seems like a reasonable guesstimate. Note in this work<sup>[4]</sup> they conclude that the reaction is not approaching the mass-transport limit on the basis of calculations made using an assumed and plausibly erroneous diffusion layer thickness of  $10\text{ }\mu\text{m}$  and they further state that the measured kinetics are insensitive to the solution being mixed on a plate which moves at a rate of  $60\text{-}90\text{ rpm}$ . Given the likely size of the particles and the low rates of mechanical mixing it does not seem likely that a diffusion layer thickness of  $10\text{ }\mu\text{m}$  is a good estimate but in the absence of better experimental data and/or information this remains ambiguous.

## Section 5: Relating Homogeneous and Heterogeneous Kinetics

As discussed in the main body of the text, in some geological articles the calcite dissolution kinetics are modelled as a homogeneous process:

$$\frac{d[\text{CaCO}_3]}{dt} = -k_c[\text{CaCO}_3](1 - \Omega)^n \quad (\text{S5.1})$$

this pseudo first order rate constant ( $k_c / \text{s}^{-1}$ ) can, if the reaction is at the surface limit, be directly related to the heterogeneous rate constant ( $k_{\text{het}} / \text{mol m}^{-2} \text{s}^{-1}$ ). Conventionally this is done using the following expression:

$$k_c = k_{\text{het}} S_g M_w \quad (\text{S5.2})$$

where  $S_g$  is the specific surface area of the material ( $\text{m}^2 \text{g}^{-1}$ ) and  $M_w$  is the calcite molecular weight ( $\text{g mol}^{-1}$ ). For an isolated spherical particle  $S_g$  can be analytically defined as:

$$S_g = \frac{3R_f}{r_p \rho} \quad (\text{S5.3})$$

Substitution of equation S5.3 into equation S5.2 yields equation 5 in the main body of the text which relates the pseudo homogeneous to the heterogeneous rate constant. Although correct the above slightly obscures the connection between these two rate constants. In the following an alternative derivation is given. We will consider the case in which the dissolution is at high undersaturation such that  $\Omega = 0$ . For a surface-controlled rate with a heterogeneous rate constant  $k_{\text{het}}$  then for a spherical particle the dissolution rate on a per particle ( $J_{\text{particle}} / \text{mol s}^{-1}$ ) basis is given by:

$$J_{\text{particle, surf}} = 4\pi r_p^2 R_f k_{\text{het}} \quad (\text{S5.4})$$

where  $r_p$  is the radius of the particle (m) and  $R_f$  is the particle roughness factor that is the ratio between the actual and geometric surface area of the particle. In order to get the total dissolution rate then equation S5.4 needs to be multiplied by the particle number density  $n$  ( $\text{m}^{-3}$ ):

$$\frac{d[\text{CaCO}_3]}{dt} = -n J_{\text{particle}} \quad (\text{S5.5})$$

$n$  for a spherical particle can be defined as:

$$n = \frac{3M_w[\text{CaCO}_3]}{4\pi r_p^3 \rho} \quad (\text{S5.6})$$

Equations S5.6 and S5.5 directly lead to the definition of  $k_c$  given in equation 5 of the main text. This result is only valid if the reaction is at the surface limit.

In contrast in the case of a mass-transport limited rate then:

$$J_{particle,MT} = 4\pi r_p D (C_{eq} - C_{bulk}) \quad (S5.7)$$

Notably this expression (equation S5.7) does not contain  $R_f$  as the mass-transport limited rate is proportional to the geometric as opposed to true surface area of the particle. Equation S5.7 and S5.5 allow equation 6 in the main text to be directly derived.

The above has considered two simple examples where the reaction is occurring at a particle that is isolated in solution. If the inter-particle separation is comparable or smaller than the extent of the diffusion layer then this assumption of isolation is not valid.

What happens if we have a relatively dense layer of particles? Let's assume we have a layer of thickness,  $L$  (m), and that a fraction,  $f$ , of the layer is filled with calcite on a volume basis and the rest is solution. If there is no transport out of this layer then the calcite will come to equilibrium with the solution in the layer leading to the solution being saturated with respect to calcite ( $C_{eq}$ ). If this layer is put in contact with a completely unsaturated seawater solution then the calcite dissolved in the layer will diffuse out of the layer. The mass-transport out of the layer is (in units of  $\text{mol m}^{-2} \text{s}^{-1}$ ):

$$j_{MT, sediment} = \frac{D_{average}(C_{eq} - C_{bulk})}{\delta} \quad (S5.8)$$

furthermore the amount of calcite depends on the depth of the layer considered:

$$\Gamma = \frac{Lf\rho}{M_w} \quad (S5.9)$$

here  $\Gamma$  is essentially an effective surface coverage and has units of  $\text{mol m}^{-2}$ .

Hence,

$$k_{c,MT sediment} = \frac{j_{MT, sediment}}{\Gamma} \quad (S5.10)$$

Equation S5.8 is expressing that the flux out of the layer is, in this model, independent of the thickness of the sediment layer being considered and so as the sediment layer gets thicker the effective homogeneous reaction rate decreases. Equation S5.10 leads directly to equation 7 of the main text. Note the effective calcite 'concentration' in the layer is:

$$[\text{CaCO}_3] = \frac{f\rho}{M_w} \quad (S5.11)$$

Hence the dissolution rate is simply,

$$\frac{d[\text{CaCO}_3]}{dt} = -\frac{D_{average}(C_{eq} - C_{bulk})}{\delta L} = -k_{c,MT sediment}[\text{CaCO}_3] \quad (S5.12)$$

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